THE STRUCTURE AND PROPERTIES OF SOME METAL DERIVATIVES OF AZO AND AZO-METHINE DYES

BY

CLAYTON FOWLER CALLIS

A. B., Central College (Mo.), 1944

M. S., University of Illinois, 1946

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R. UNIV. BIBLIOTHEEK LEIDEN

THE STRUCTURE AND PROPERTIES OF SOME METAL DERIVATIVES OF AZO AND AZO-METHINE DYES

Introduction

The importance of the formation of metallic lakes in the dyeing of cloth was recognized many, many years ago, because the reaction of dyes with metallic salts usually improves their fastness to washing and rubbing, as well as to light, and often produces more desirable shades. However, only in very recent times have these metallic lakes been regarded as typical coordination compounds. Very little information is available as to their exact structure, although in some cases the ratio of metal to combined dye has been reported. In considering the mechanism of dyeing on various fibers, it would be of considerable advantage to know more about the structure and properties of these coloring lakes.

In this investigation, cobalt complexes of the simplest types of mono-ortho substituted and di-ortho substituted azo and azo-methine dyes were prepared and studied by analytical and physical methods. For the purposes of comparison, similar lakes of divalent zinc and trivalent chromium were also investigated. From the facts that were established in this investigation, and on the basis of data already published in the literature, a general theory of the coordination of azo dyes is advanced and discussed.

Theoretical and Discussion of Results

The special properties and increased stability of the metallic lakes of azo dyes containing the hydroxyl, carboxyl or amino-group in an ortho-position to the azo-nitrogen atoms have been attributed to the formation of a ring structure involving the metal atom, the azo-nitrogen atoms and the

ortho-substituent. Drew and Landquist (1) were unable to obtain metallic lakes in which the metal atom was coordinated to the azo-nitrogen atoms unless the metal atom was attached by a covalent bond to substituents in the ortho-position to the azo group. Hydroxyl groups in the meta or para positions were found to have little or no effect.

Molecules of the di-ortho substituted type are known to form coordination compounds with a number of metals more readily than mono-ortho substituted ones, and the complexes that are formed are considerably more stable. Morgan and Main Smith (2) felt that only one of the ortho-substituted groups was attached to the metal, but Drew and Landquist were of the opinion that this phenomenon can best be explained by assuming that the metal combines with both of the ortho-substituted groups and the azo-nitrogen atoms. The structure of such a lake would involve a fused-ring system of one five-membered and one six-membered ring.

The cobalt lakes present some interesting theoretical problems because the cobalt can be stabilized in both the divalent and trivalent states. Magnetic measurements on the product obtained from the reaction of cobaltous chloride with 2′-hydroxybenzal: 2-hydroxy-5-chloroaniline in ammoniacal alcoholic solution indicate that a mixture of complexes of both divalent and trivalent cobalt are formed. Direct methods for preparing complexes of this metal in the two valence states were studied.

The cobaltous 1:1 dye:cobalt complex of this azo-methine dye was prepared from the reaction with cobaltous acetate in alcoholic solution in an atmosphere of nitrogen. Evaporation of the filtrate in a stream of air gave a darker red-brown cobaltic complex. Although the material apparently was not obtained pure, these results indicate a 3:1 dye:metal ratio. In order to formulate this lake, it must be assumed that one of the hydroxyl groups is not attached to the cobalt. This same experiment was repeated by mixing the constituents in air. The same products were isolated in both

cases, but when the nitrogen atmosphere was used, a much higher yield of the cobaltous 1:1 dye:cobalt complex, and a lower yield of the red-brown cobaltic complex was obtained.

The reaction of cobaltous chloride hexahydrate with this dye has been found to give a very poor yield of a cobaltous complex (3) containing one cobalt for each dye residue. The yield was considerably greater with cobaltous acetate, but was still only about half the theoretical.

The cobaltic complexes were prepared by replacement reactions in 2N ammonium hydroxide using hexammine cobaltic chloride, bis-diethylenetriamine cobaltic chloride, and sodium cobaltinitrite as the source of the trivalent cobalt. It was thought that such replacement reactions would be advantageous in preparing complexes of cobalt in the trivalent state, free of any divalent material. It was also hoped that such procedures could be used to control the presence of groups other than dye molecules in the coordination sphere. Such groups may be points of attack for the disintegration of the whole molecule.

A 3:1 dye:cobalt complex was prepared from the reaction of hexammine cobaltic chloride and benzeneazo-β-naphthol in 50% alcohol. Apparently all of the ammonia was liberated and the six coordination positions filled by the dye molecules. Complexes containing three dye residues and three ammonia molecules for each two cobalt atoms was obtained from hexammine cobaltic chloride and sodium cobaltinitrite with 2′-hydroxybenzal: 2-hydroxy-5-chloroaniline. A structure of the type [Co dye $(NH_3)_3$] [Co dye_2] is proposed for these complexes. A similar 2:3 chromium:dye complex containing only two molecules of ammonia for two cobalt atoms was obtained from hexammine chromic nitrate. The reactions of a bifunctional dye molecule with a trivalent metal are not as clear cut as in the case of a divalent metal since the dye can satisfy only two of the three primary valences.

A water soluble complex [Co (diethylenetriamine) dye]

Cl, containing one dye and one diethylenetriamine molecule for each cobalt atom with the chlorine as an ion, was prepared from the reaction of 2′-hydroxybenzal: 2-hydroxy-5-chloroaniline with bis-diethylenetriamine cobaltic chloride. This means that this particular replacement reaction must occur in steps, the first step being the replacement of one diethylenetriamine molecule by one dye molecule. Each molecule coordinated to the cobalt in this complex can satisfy three coordination positions. The three primary valences are taken up by the bifunctional dye molecule and the ionic chlorine.

Similar 2:3 metal:dye complexes were prepared by Morgan and Main Smith (2) from di-ortho hydroxy azo dyes. These investigators postulated that three dye molecules react with one cobalt atom and displace all of the ammonia from its coordination sphere; and a second or third pentammine cobaltic radical with all of the ammonia that it originally held forms a salt with the other ortho-hydroxyl group. The present work and the work of Drew and his students (1, 4-6) does not confirm this view. If the reaction of bis-diethylenetriamine cobaltic chloride with 2′-hydroxybenzal: 2-hydroxy-5-chloroaniline had gone as Morgan would postulate, there should be two diethylenetriamine and three dye molecules for every two cobalt atoms. But the ratio found was one cobalt for each dye. Morgan also postulated that a pentammine cobaltic radical formed a salt with the second hydroxyl group in a di-ortho hydroxy azo dye. If this theory is correct, then an ion such as $[Co(NH_3)_5SCN]^{++}$ or $[Co(NH_3)_4(SCN)_2]^{+}$ that is carrying a smaller charge, would combine in a different ratio with the salt-forming group and the resulting lake would contain one sulfur atom for each two cobalt atoms. Such an experiment was tried using thiocyanatopentammine cobaltic chloride and 2′-hydroxybenzal: 2-hydroxy-5-chloroaniline. The same 2:3 cobalt:dye lake formed in the reaction of hexammine cobaltic chloride with the dye was precipitated. Qualitative tests for sulfur gave negative results. All of the thiocyanato groups were un-

doubtedly replaced.

These experimental results tend to support the theory that the replacement reactions occur in steps. If a di-ortho hydroxy azo dye satisfies two primary valences and three secondary valences of a metal such as cobalt or chromium, then a 1:1 dye: metal complex would carry a positive charge and a 2:1 dye: metal complex a negative charge. A 2:3 dye: metal complex is formulated as a combination of two oppositely charged groups.

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VITA

The author was born in Sedalia, Missouri, on September 25, 1923. He received his elementary and high school education in the consolidated schools of Hughesville, Missouri. In February, 1944, he received the degree of Bachelor of Arts with a major in chemistry from Central College, Fayette, Missouri. From February, 1944, to March, 1945, he was employed as an instructor for Navy V-12 students at Central College. In the fall of 1945, he entered the Graduate School of the University of Illinois. He held a research assistantship established at the University by the General Aniline and Film Corporation from March, 1946, to June, 1947. At this time he was awarded the Du Pont Fellowship which he still holds. He received the degree of Master of Science in Chemistry from the University of Illinois in September, 1946.

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